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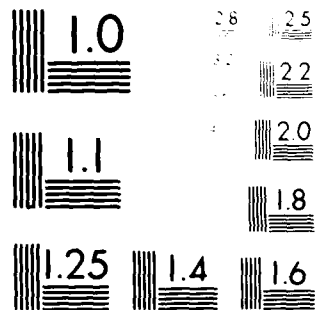
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(6) (13)  $^{13}\text{C}$  NMR of  $\text{AsF}_5$  Doped Polyacetylene.

by

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$^{13}\text{C}$  NMR STUDY OF  $\text{AsF}_5$  DOPED POLYACETYLENE

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ABSTRACT: Natural abundance  $^{13}\text{C}$  NMR experiments using cross polarization and magic angle spinning are reported for polyacetylene as a function of  $\text{AsF}_5$  doping level. In contrast with previous authors we find that the doping of *cis*-polyacetylene leads, even at low doping levels, to a new signal characteristic of the doped regions of the polymer. Similar measurements on *trans*-polyacetylene indicate that the doping of the *trans* isomer proceeds considerably more uniformly than that of the *cis* isomer. Comparisons with appropriate model compounds suggest that the observed shift of the  $^{13}\text{C}$  NMR signal on doping is primarily a chemical shift rather than a Knight shift.

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In an attempt to resolve the current controversy regarding the changes in magnetic susceptibility in polyacetylene as a function of doping,<sup>1,2</sup> Peo et al. have examined the  $^{13}\text{C}$  NMR spectra of  $\text{AsF}_5$  doped polyacetylene samples using magic angle spinning.<sup>3</sup> In a study limited to *cis*-(CH)<sub>x</sub>, they reported no substantial change in the  $^{13}\text{C}$  spectrum up to a doping level of ~7 mole %, at which point a rather abrupt change to a broad, downfield-shifted line was observed. The authors attributed this change to a Knight shift and correlated the result with the sudden increase in Pauli susceptibility observed at ~7% doping in Schumacher-Slichter measurements.<sup>2</sup> However, several puzzling aspects of the Peo data led us to reexamine their results and extend the study to *trans*-polyacetylene. Particularly disturbing was their failure to observe even a chemical shift in the (CH)<sub>x</sub> spectrum for doping levels below 7%, despite the fact that doping is believed to remove charge from the polymer  $\pi$ -system.<sup>4</sup>

Polyacetylene for our experiments was prepared by the procedure of Ito et al.<sup>5</sup> Conversion of *cis*-polyacetylene to the *trans* isomer was carried out under ~0.5 atm of helium at 200°C for one hour. The  $\text{AsF}_5$  was purified as described earlier.<sup>6</sup> Doping of the polyacetylene was performed as described in the work of Ikehata et al.<sup>2</sup> Final compositions were determined by weight uptake. All manipulations of the polymer were carried out either on a vacuum line or in an inert atmosphere dry box. In particular, the NMR sample rotors were loaded in the dry box and transferred to the spectrometer under argon. Undoped samples were cut into small pieces before being packed in the rotors; doped samples were cut and dispersed by grinding with glass powder before loading. An undoped *cis* sample was also cut and ground to ensure that no sample degradation or *cis-trans* isomerization occurred on grinding. During the acquisition of data the sealed rotors were under a constant flow of helium. Spectra were obtained in a magnetic field of

15 kOe using cross polarization and magic angle spinning techniques. Shifts are expressed in ppm with respect to tetramethylsilane (TMS).

Figure 1 shows our results for the doping of *cis*-(CH)<sub>x</sub>. The bottom spectrum is that of the undoped starting material. The main peak at 127 ppm corresponds to *cis* material; the low-field shoulder (~136 ppm) is due to the presence of a small amount of the *trans* isomer.<sup>3,7,8</sup> The top spectrum shows the same material after doping to a composition of [CH(AsF<sub>6</sub>)<sub>0.068</sub>]. As in the Peo data<sup>3</sup> a very broad resonance centered at ~150 ppm is observed. The origin of this downfield shift in the doped polymer is discussed in detail below.

The middle spectrum in Figure 1 shows a *cis* sample doped to the intermediate concentration of 3 mole %. Superficially, this spectrum resembles those presented by Peo et al. for intermediate doping levels: a sharp and apparently unchanged *cis* line as well as a slightly larger *trans* shoulder are readily evident. However, in contrast to the Peo results, we find that these peaks lie on top of a rather broad peak shifted downfield to a position characteristic of the doped polymer. This feature is more apparent in the expanded spectrum of the 3% sample shown in Figure 2. This broad peak, smaller in relative intensity, is also found in a 1% doped *cis* sample (Figure 3).

Figure 4 shows comparable data for AsF<sub>5</sub> doped *trans*-(CH)<sub>x</sub>. (For experimental reasons only a 5% lower limit on the composition of the heavily doped sample could be determined.) The heavily doped sample exhibits a spectrum quite similar to that of 7% AsF<sub>5</sub> doped *cis*-polyacetylene. However, the spectrum of the 3.2% *trans* sample is quite dramatically changed from that of the undoped *trans* material, and appears to consist of a

somewhat broadened peak at the original *trans* position lying on top of the broader downfield signal characteristic of the heavily doped material.

From these data we draw several conclusions: 1) Low levels of doping do not lead to extensive conversion of *cis*-polyacetylene to the unoxidized *trans* isomer. 2) In contrast to the results of Peo et al., however, signals characteristic of the doped polymer can be seen in the spectrum of  $\text{AsF}_5$  treated *cis*-polyacetylene at doping levels as low as 1%. Whether these signals correspond to material which is *cis* or *trans* in nature cannot be answered directly by these experiments; the observation of very similar spectra for heavily doped *cis* and *trans* material is consistent with previous suggestions that the doped material is very likely *trans*.<sup>9</sup> 3) In the first  $^{13}\text{C}$  NMR examination of  $\text{AsF}_5$  doped *trans*-(CH)<sub>x</sub>, we find that 3% doping causes a distinct broadening of the original *trans* line as well as the onset of the broad downfield signal centered at ~150 ppm. In contrast, the spectrum of a 3% doped *cis* sample looks essentially like a superposition of the signals of undoped *cis* and heavily doped *cis*. Together these results suggest that the doping of *cis*-(CH)<sub>x</sub> is considerably less uniform than that of *trans*-(CH)<sub>x</sub>. Even the *trans* doping, however, does not appear to be completely uniform.

The downfield shift in the doped polyacetylene has been explained as a Knight shift.<sup>3</sup> However, the position of this signal is comparable to the shifts observed for the carbons of delocalized  $\pi$ -carbonium ions where no conduction electrons are present. For example, although the  $^{13}\text{C}$  NMR of benzene exhibits a sharp singlet at 128.7 ppm,<sup>10</sup> the signal of the tropylium ion, which contains one positive charge equally distributed over seven carbon atoms, is shifted to 155.3 ppm.<sup>10</sup> (Determination of the charge per carbon in doped (CH)<sub>x</sub> is complicated by the obvious inhomogeneity of the doping. Motion of

the already delocalized charge site would also lead to averaging on the NMR time scale.) We suggest that the primary contribution to the downfield shift on doping is the chemical shift arising from the removal of electrons from the  $\pi$ -system, and that any Knight shift represents a smaller contribution superimposed on this chemical shift. Moreover, since the conduction electrons in this system must be  $\pi$ -electrons, the Knight shift must involve core polarization, orbital and/or dipolar coupling; in particular both the magnitude and direction of such a shift are uncertain.<sup>11</sup>

The situation is further complicated by the current uncertainty over the interpretation of magnetic susceptibility studies on  $\text{AsF}_5$  doped polyacetylene, particularly in the intermediate doping regime ( $\sim 1-7\%$ ). Schumacher-Slichter measurements on the same 3.2% doped *trans* sample used in the above  $^{13}\text{C}$  NMR experiments show a low Pauli susceptibility of  $\sim 1.5 \times 10^{-7}$  emu/mole, while EPR studies on this sample yield a Pauli susceptibility of  $\sim 1 \times 10^{-6}$  emu/mole.<sup>12</sup> Since any Knight shift should correlate with the Pauli spins, an independent resolution of the susceptibility problem will be required before a realistic estimate of the Knight shift contribution to the observed spectra can be made.

#### ACKNOWLEDGMENTS

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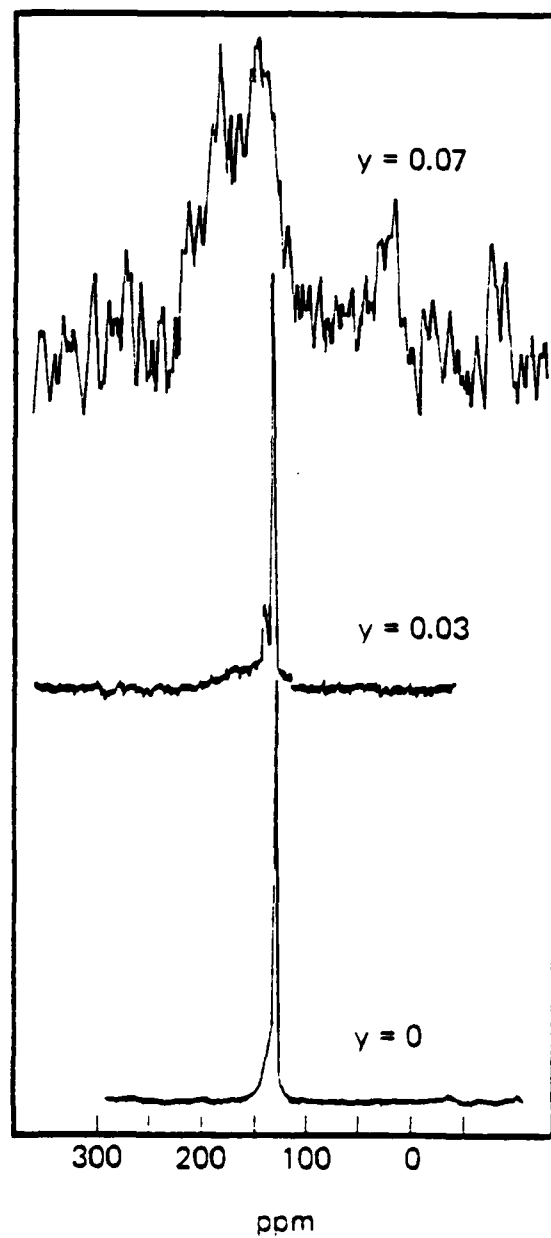


Figure 1.  $^{13}\text{C}$  NMR spectra of *cis*-polyacetylene before (bottom) and after doping with  $\text{AsF}_5$  to composition  $[\text{CH}(\text{AsF}_6)_y]$

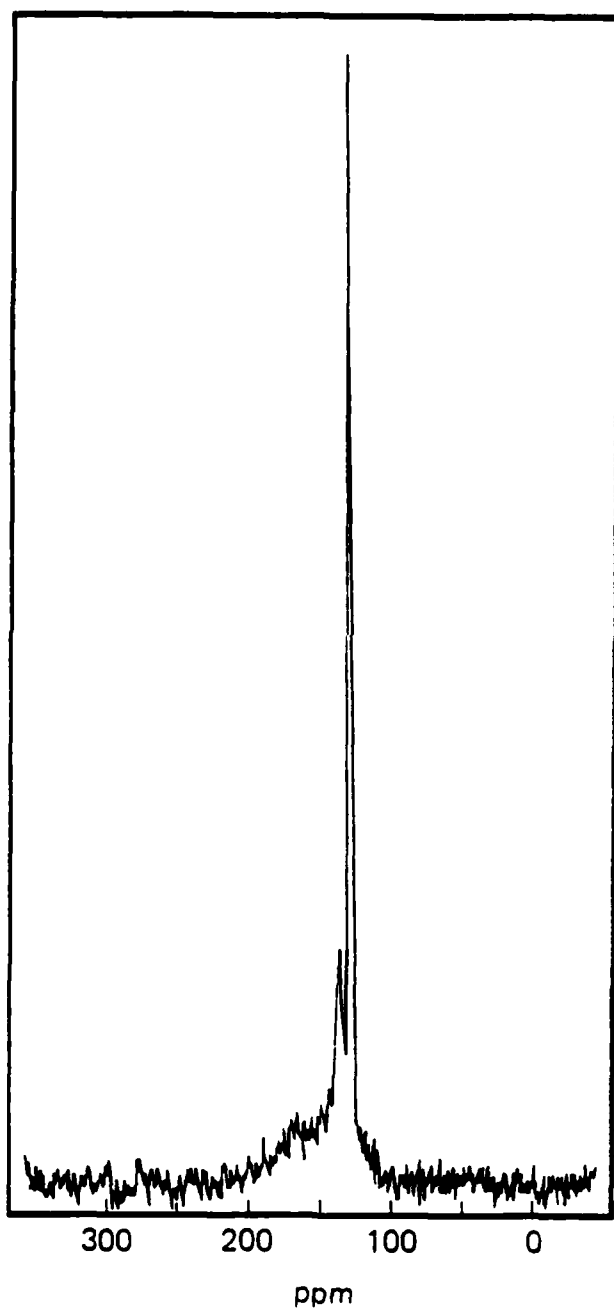


Figure 2. Expanded  $^{13}\text{C}$  NMR spectrum of  $[\text{CH}(\text{AsF}_6)_{0.03}]$ .

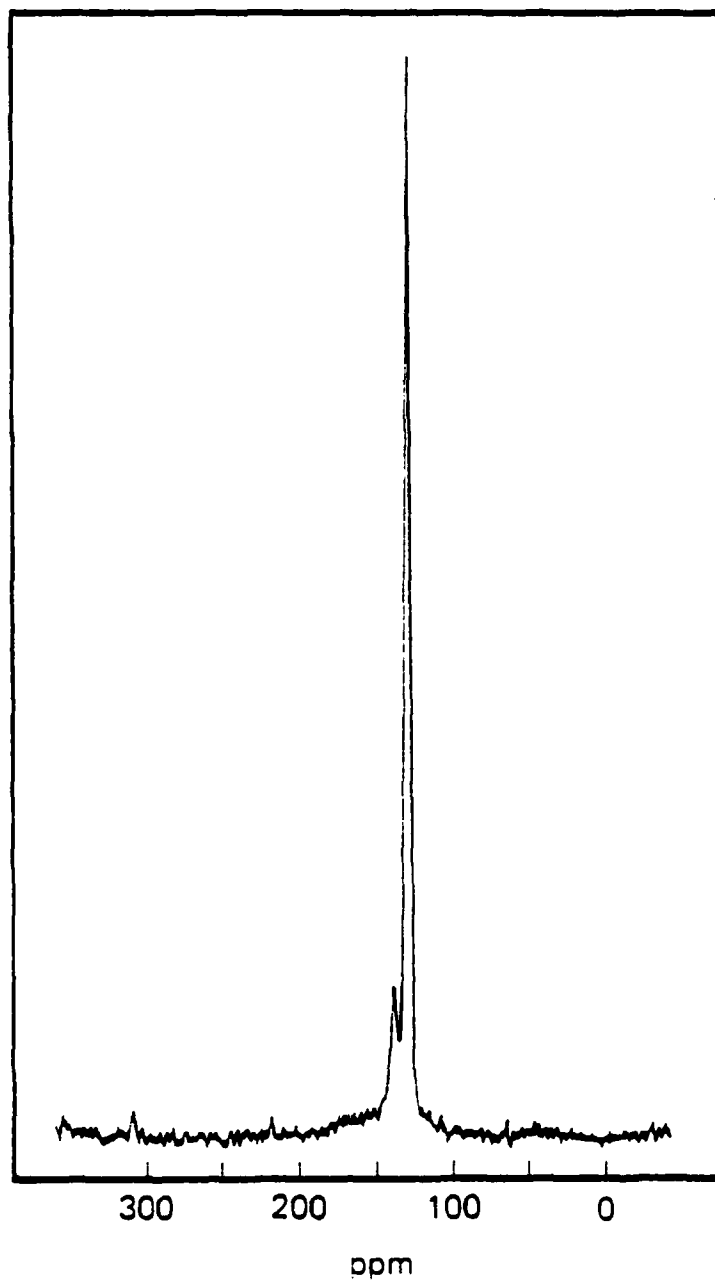


Figure 3. Expanded  $^{13}\text{C}$  NMR spectrum of  $[\text{CH}(\text{AsF}_6)_{0.01}]$ .

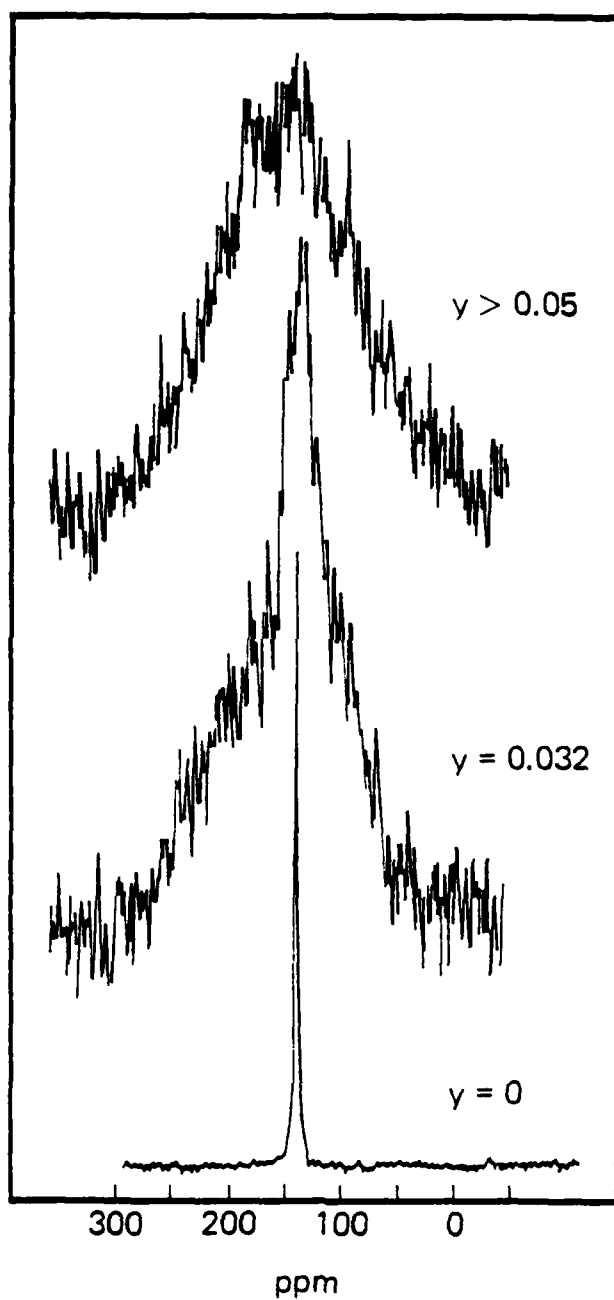


Figure 4.  $^{13}\text{C}$  NMR spectra of *trans*-polyacetylene before (bottom) and after doping with  $\text{AsF}_5$  to composition  $[\text{CH}(\text{AsF}_6)_y]$ .

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